1,091,049

PATENT SPECIFICATION

NO DRAWINGS

1091049

Inventor: CARL REGUTTI

Date of Application and filing Complete Specification: Nov. 23, 1964.

No. 47642/64.

Complete Specification Published: Nov. 15, 1967.

Index at acceptance:—D2 B(4, 6, 10, 13F, 13JX, 13X, 15)

Int. Cl.:—D 21 h 5/22

COMPLETE SPECIFICATION

Bacteriostatic Paper and the manufacture thereof

We, CALGON CORPORATION, a Corporation organized under the laws of the State of Pennsylvania, United States of America, of P.O. Box 1346, Pittsburgh, Pennsylvania 15230, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to bacteriostatic paper, and the manufacture thereof. In particular, it relates to tissue paper having incorporated therein a small amount of an alkyl-substituted guanadine salt, in which the alkyl group contains 10 to 16 carbon atoms, as a microorganism inhibitor.

Prior to the present invention, no commercially successful tissue paper for inhibiting microorganisms was known. Absorptive bacteriostatic tissue paper is desirable for the prevention of the spread of disease bacteria and other undesirable microorganisms and to inhibit the growth not only of pathogens but of bacteria which produce objectionable odors, stains, and the like. Such papers are particularly suitable for the manufacture of dental, hospital and professional towels, gowns, wipes, baby diapers and the like.

Tissue paper generally lacks the strength and coherence to permit it to be dipped, sprayed, or otherwise effectively treated with the solution after it has been formed and/or dried. Moreover, even if nondestructive spray techniques or other methods of surface application of chemicals to dry formed tissue paper were developed, the problems of satisfactory adherence of the chemical to the paper and heat-stability would still remain. Such methods of application are not likely to provide uniform distribution of chemical throughout the thickness of the paper since it is applied mainly to the surface.

On the other hand, conventional bacteriostatic agents have not been successfully applied in the various wet stages of paper manufacture, primary because such agents are likely to be almost entirely lost from the fibres during the agitation steps and from the wet or newly formed sheet in the various draining and pressing steps preliminary to drying. Many convention bactericides are unsuitable for application in paper-making systems because of properties such as excessive foaming, staining and odor. Tissue paper, paper diapers, toilet paper, sanitary napkins, and the like must not contain toxic or irritating materials, and many conventional bactericides are unsuitable because of their toxicity to humans. This invention is useful for all the above applications, as well as many other which will be obvious to men skilled in the art.

The method of the invention contemplates the use of a microorganism-inhibiting agent exhibiting substantivity to the fibres of tissue paper so that it may be introduced to the pulp slurry or stock solution prior to the formation of the sheet or sprayed onto the pulp during formation of the sheet, and will remain a more or less permanent part of the fibre structure evenly distributed throughout. This invention comprises adding a small amount of an alkyl-substituted guanidine salt in which the alkyl group contains 10 to 16 carbon atoms to the stock suspension prior to formation into a sheet. Such alkyl-substituted guanidine salts as hereinafter described will be referred to hereinafter simply as alkyl-guanidine salts. They include salts such as the sulfate, carbonate, phosphate, oxalate, malate, and chloride. The chloride salt is often referred to as the hydrochloride, and the salts generally as acid salts. An alkyl-guanidine chloride and an alkyl-guanidine hydrochloride are different names for the same thing.

Generally, the guanidine salt is preferably added at the beginning of the paper-making process, as, for example, to a Hi-Low pulper although it may be added at any time prior to conversion; for example, it may follow the bleaching step and precede the pickup by the

[*Price 4s. 6d.*]

Fourdrinier screen or other sheet-forming apparatus. The basic guanidine structure is not adversely affected by bleaching, however. The stock suspension which has been substantially prepared for formation into a sheet is referred to herein as the "prepared tissue-paper stock suspension." It may be washed, lapped and dried, diluted, agitated, beaten, bleached, transported, and/or otherwise treated after the addition of the alkyl-guanidine salt; the suspended fibres themselves, however should be substantially ready to be formed into a sheet prior to the addition. Any chemical treatment which does not substantially affect the chemistry of the fibres may be employed after addition of the alkyl-guanidine salt. The prepared stock suspension may be formed from a dried pulp of the type available in commerce for use by paper mills which are not associated with pulp mills. The dried pulp may be already treated with the alkyl-guanidine derivative; i.e. the guanidine derivative may be added to the stock suspension in the pulp mill after the fibres have been otherwise prepared for formation into a sheet although they are subsequently dried for shipment to a paper mill. A prepared tissue-paper stock suspension is a suspension of fibres which has already passed through the digester and blow-tank steps, if such steps are employed, and is substantially capable of being formed into a sheet, although it may be dried first instead. It may or may not be bleached. The optimum point of addition will vary depending on the beating process, holding time, alum, bleach, or other chemical treatment, pulp consistency, temperature, mixing time, and other variables before or after addition of guanidine salt. Generally, however, the preferred method of adding is to the pulper water before charging with pulp. This provides a dilute solution into which the pulp is charged and appears to give the most efficient use of the alkyl-guanidine salt.

Among the alkyl-guanidine salts which are useful in the invention are those in which the alkyl group contains about 12 to 14 carbon atoms. Some slight effects may be found by using alkyl-guanidine salts in which the alkyl group contains 10 to 16 carbon atoms but these effects generally are much less significant than with 12 to 14 carbon atoms. Specific examples are tetradecyl-guanidine acetate, dodecyl-guanidine hydrochloride, hexadecyl-guanidine sulfate, and decyl-guanidine lactate. The compound may be added to the prepared stock solution in the form of an aqueous or other solution or suspension or in the anhydrous state. Dodecyl-guanidine hydrochloride (DGH) is one of the more water-soluble and also one of the more effective compounds and is preferred in the invention. The compound should be added to the stock suspension far enough in advance of the Fourdrinier screen or other sheet-forming device, depending on the method of addition and other system variables, to ensure even and complete distribution. The presence of soluble chlorides or of the chloride ion appears to improve the effectiveness of alkyl-guanidine salts. The chloride ion can help keep dodecyl-guanidine hydrochloride dispersed in systems containing high contents of sulfate, silicate, acetate, phosphate, and other such ions (which tend to decrease the solubility or dispersibility of DGH and make it less effective in certain applications). The following examples illustrate the invention:

Example I.

Four batches of pulp were made and treated as follows. Two thousand pounds of dry digested and bleached pulp were added to 4,000 gallons of water to make a slurry containing about 6% pulp by weight in a Hydropulper. To this, 10 pounds of wet-strength resin and a small amount of alum were added to make a preprepared tissue-paper stock solution, and 12 pounds of a 25% aqueous solution of dodecyl-guanidine hydrochloride (DGH) were added to the hydropulper. The slurry was then diluted to about 0.1% pulp consistency and then formed into a sheet on a Fourdrinier screen. It was dried on a Yankee drier at about 180°F.—212°F. for about five seconds. A control batch was made identical to the treated tissue with the exception that DGH was not added.

After the tissue had been completely dried, sample discs were taken and placed on bacterial media inoculated with staphylococcus aureus to perform the zone of inhibition test described in United States of America Federal Specification UU—P—510, Paper Sheeting, Bacteriostatic 4.4.2. The eight samples of 4-ply tissue paper (two from each DGH-treated batch) exhibited approximately ½ mm inhibition zones. No growth occurred under the discs. The control exhibited no inhibtion zone and considerable bacterial growth was observed beneath the disc Tests for DGH in the paper were made following the general method of Kjeldahl for nitrogen. Based on this test, the paper contained an average of 219 ppm of DGH.

The same tissue paper was subjected to the "sanitizing activity" test No. 100—1961T of the American Association of Textile Chemists and Colorists entitled "Antibacterial Finishes on Fabrics". "Sanitizing activity" is defined as the ability of material not only to inhibit bacterial growth, but also to reduce the number of bacteria present on the material by killing them. After two hours, the DGH-treated tissue paper had 53.6% fewer bacteria (of an original inoculum of staphylococcus aureus ATCC No. 6538) than the untreated control, and after 6½ hours the DGH-treated tissue exhibited 98.9% fewer bacteria than the control.

Example II.

Into a 150 hp Jones Hi-Low pulper, operating at 880 rpm, 3,400 gallons of clarified white water were added. Seven pounds of

"Biocheck 60" (25% DGH), as delivered were added and mixed thoroughly for one minute. Next 2,000 pounds of dry lapp pulp (70% bleached Kraft and 30% sulfite) were charged into the pulper. This mixture was violently agitated for 7 minutes. Then the pulp slurry was dropped into a holding chest (non-operating refining chest). Another 3,400 gallons of water (pulper capacity) was added to the pulper. This water was used to flush the pulper and then added to the original charge in the holding chest. The pulp consistency in the holding chest was approximately 3.5%.

Next 0.5% based upon the fiber weight of a neutral-curing type wet strength resin (Kymene 557; the word "Kymene" is a registered Trade Mark) and a direct dye were added to the holding chest. After a period of mixing, the slurry was passed through a machine Jordan. By means of a consistency regulator, the furnish was brought to a consistency of approximately 0.1%.

Prior to the Jordan the pulp slurry had a Canadian Standard freeness of 700 cc. at 20°C. After the Jordan, the freeness was 500 cc. at 20°C.

The 0.1% slurry passed into a pressurized Beloit head box and onto a conventional Fourdrinier wire (speed 1,500 fpm). The web was carried by a pick-up felt and directly transferred the face of a 10 ft.-diameter Yankee drier. Then the dry tissue was pressed into a 4-ply product through a non-heated calender.

Bacteriostatic tissue made in this fashion passed United States of America Federal Specification UU—P—510; Bacteriostatic Paper Sheeting. In addition to making the paper effectively anti-bacterial, the extra benefit of making the paper softer also resulted from DGH application.

Example III.

Hand sheets were prepared from pulp stock of 60% sulfate and 40% sulfite blend to which were aded various alkyl-guanidine salts of varying chain lengths at a concentration of 0.5% based on fiber weight. A wet-strength resin, Kymene 557 and an optical brightener were added to come portions. Solidified Tryptone Glucose Extract agar (TGE) plates weer added to some portions. Solidified micrococcus aureus, FDA 209. Discs were cut from each hand sheet and placed on this inoculated agar. These plates were refrigerated at 5°C. for 18 hours and then incubated for 24 hours at 34.5° C. After incubation, the discs were examined for zones of inhibition.

TABLE I

Testing the Bacteriostatic Properties of Paper Pulp Mats Treated with Various Alkyl-Guanidine Salts

ALKYL-GUANIDINE DERIVATIVE	Stock	Water	Inhibition Zones (mm)
n-Decyl-guanidine hydrochloride	A[1]	Tap	Slight
" " acetate	A	Tap	Slight
" " glycolate	A	Tap	Slight
" " lactate	A	Tap	Slight
n-Dodecyl-guanidine hydrochloride	B[2]	Tap	2
" " acetate	B	Tap	2
" " acetate	B	Distilled	2
" " acetate	A	Distilled	0
" " acetate	A	Tap	0
" " malate	A	Tap	2.5
" " nitrate	A	Tap	2.5
" " phthalate	A	Tap	1
" " sulfate	A	Tap	2
" " sulfate	A	Distilled	0
" " sulfate	C[3]	Distilled	1 (1/2 disc)
" " carbonate	C	Tap	2
n-Tetradecyl-guanidine hydrochloride	A	Tap	0.5-1
" " acetate	A	Tap	0.5-1
" " glycolate	A	Tap	0.5-1
" " lactate	A	Tap	0.5-1
n-Hexadecylguanidine hydrochloride	C	Tap	Slight
" " hydrochloride	A	Distilled	Slight
" " acetate	C	Tap	Slight
" " cyclamate	C	Tap	Slight
" " lactate	C	Tap	Slight
" " sulfate	C	Tap	Slight

1. — A 40% sulfite/60% sulfate blend
2. — B " " + Kymene 557
3. — C " " " %optical brightner

EXAMPLE IV

Into a hydropulper was placed white water, followed by ten pounds of "Biochek 60" (25% DGH) and mixed thoroughly for several minutes. Next 1500 pounds of dry virgin pulp (sulfates and sulfites) and 300 pounds of broke were charged into the hydropulper, giving a pulp consistency of about 4.5%. This mixture was agitated, with recirculation, as violently as possible for 30 minutes. Then pitch-dispersants, fluorescent dyes, and re-wetting agents were added and mixed. This pulp slurry was dropped into a refining chest, recycled for 25 minutes, and 150 pounds of fibrous filler was added. Next, alum was added and this slurry dropped into the machine chest. From there the pulp slurry passed into a consistency regulator, was diluted with white water, and proceeded into a disc-refiner head box to which was also added wet-strength resin. After passing through the disc refiner, this dilute slurry entered the machine head box, to which were added antifoaming agents, and then onto a Fourdrinier wire. The web was dried on a Yankee drier at an 18% crepe. Not only did the finished tissue paper product exhibit significant anti-bacterial properties by "zone of inhibition" test methods, but the undesirable musty odor normally characteristic of this paper had been significantly diminished by the DGH treatment.

Other tests using bacteria responsible for causing diaper rash through degradation of urine to ammonia revealed that paper made

with alkyl-guanidine hydrochlorides of C_{12}, C_{14}, and C_{16} alkyl-chain lengths could effectively inhibit growth and subsequent urine degradation by such organisms.

Laboratory tests have shown that the effectiveness (based on fungistatic, bacteriostatic or bactericidal properties) of the treatment is generally related to the amount of DGH in the paper and that the amount of DGH in the paper is generally proportional to the amount added to the stock suspension, all other factors being equal. A small amount of DGH appears to be effective to some degree although the effectiveness of very small amounts varies somewhat with the test procedure. So far as the applicants are aware, there is no minimum amount below which DGH is totally without a bacteriostatic effect, nor is there an upper limit of concentration which is completely ineffective. The preferred practice, however, is to maintain a level of 0.0015% to .10% of alkyl-guanidine salt in the pulper water at the time the pulp is added or alternatively 0.05% to 3% preferably 0.1% to 1%, on the dry weight of pulp added. A preferred amount on the finished tissue is 0.05% by weight in the case of dodecyl-guanidine hydrochloride.

WHAT WE CLAIM IS:—

1. A bacteriostatic tissue paper which contains a small amount of an alkyl-substituted guanidine salt, in which the alkyl group contains 10 to 16 carbon atoms.

2. A bacteriostatic tissue paper according to claim 1, wherein said alkyl group contains 12 to 14 carbon atoms.

3. A bacteriostatic tissue paper according to claim 1 or 2, wherein the salt is a hydrochloride.

4. A bacteriostatic tissue paper according to any of the preceding claims, wherein the salt is dodecyl-guanidine hydrochloride.

5. A method of making bacteriostatic tissue paper which comprises forming a tissue-paper stock suspension, including an alkyl-substituted guanidine salt, in which the alkyl group contains 10 to 16 carbon atoms, in the stock suspension, and forming the stock into a sheet.

6. A method according to claim 5, in which the alkyl-substituted guanidine salt is added to the water forming the vehicle for the suspension prior to the addition of pulp to form the paper stock suspension.

7. A method according to claim 5 or 6, in which a source of chloride ion is added to the suspension.

8. A method according to any of claims 5 to 7, in which the alkyl-substituted guanidine salt is added in an amount equal to from 0.1% to 1% on the weight of the pulp.

9. A bacteriostatic tissue paper substantially as hereinbefore described with reference to the examples.

10. A method of making bacteriostatic tissue paper substantially as hereinbefore described with reference to the examples.

STEVENS, LANGNER, PARRY
& ROLLINSON,
Chartered Patent Agents,
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.
—1967. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2,
from which copies may be obtained.